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(54) **ANTIBACTERIAL POLYCARBONATE COMPOSITE MATERIAL AND PREPARATION METHOD THEREFOR**

(57) The present invention discloses an antibacterial polycarbonate composite, which includes the following components in parts by weight: 100 parts of a polycarbonate, 0.01 - 5 parts of a nanometer metal oxide, and 0.01 - 5 parts of a silicon-containing high-molecular polymer; and based on a total weight of the antibacterial polycarbonate composite, a content of a silver ion is 100 - 1200 ppm. In the present invention, through a dispersion and migration effect by synergizing the nanometer metal oxide and the silicon-containing high-molecular polymer,

a concentration of the silver ions is progressively increased from inside to a surface in the material, and as the surface of the material is attrited, the silver ions inside the material will migrate to the surface at an even rate along with the silicon-containing high-molecular polymer, making the material maintain a well sustained antibacterial effect, which can reduce an added amount of the silver ions, with advantages of a good appearance, a good color stability, and a good antibacterial performance, etc.

Description**TECHNICAL FIELD**

5 [0001] The present invention relates to the technical field of polymer composites, and particularly relates to an anti-bacterial polycarbonate composite and a preparation method thereof.

BACKGROUND

10 [0002] At present, polycarbonate (PC) is widely used in production of a variety of industrial and civil parts (such as a variety of transparent parts, lampshades, and instrument panels, etc.). With an improvement of living standards, people are paying more and more attention to health. In order to avoid bacterial reproduction in parts made of plastics and improve safety of products, requirements for plastics to inhibit the bacterial reproduction are becoming more and more stringent.

15 [0003] At present, antibacterial agents which are widely used in modified plastics are metal ion antibacterial agents. Because of their instability, these metal ions are easy to be oxidized in processing and even in use, not only causing loss of a bactericidal function but also darkening the color of materials. Especially in engineering plastics, such as polycarbonate resin, a processing temperature is often higher than 300°C, so it is greatly difficult to make the antibacterial agent stable and maintain an effect in a relatively high-temperature processing technology. In the prior art, an appearance 20 can be modified by increasing an amount of color powder, but increasing the amount of the color powder will greatly increase a cost of the material and directly affect a heat-resistance performance of the polycarbonate material. A yellowing-resistant nanometer silver antibacterial polycarbonate material is disclosed in Chinese patent 201610555237.5, which uses a metal ion passivator to prevent the material from yellowing at high temperature in the processing, but does not take dispersion problem of silver ions in the material into account.

25 [0004] At the same time, the melt polycarbonate has a high viscosity in the processing, and the polycarbonate material is a temperature-sensitive material rather than a shear-sensitive material, so a filling-type metal ion antibacterial agent is easy to aggregate. In the case of less added amount and obvious gradient concentration difference in a matrix, how to ensure that the antibacterial agent provides a bactericidal effect when dispersed on a surface of the whole material 30 becomes an urgent technical problem to be solved. Moreover, in the prior art, the silver ion antibacterial agent is only enriched on the material surface or uniformly dispersed in the material. As for the former, it is easy to lose an antibacterial effect because of attrition of the material surface; as for the latter, the silver ion antibacterial agent which is distributed on the surface is very few because the silver ion antibacterial agent is uniformly distributed in the material, so the antibacterial effect is not good. A solution is generally to increase an amount of the silver ion antibacterial agent, thereby increasing the cost. On the other hand, after the silver ion antibacterial agent on the material surface is attrited, the silver 35 ion antibacterial agent present inside the material cannot migrate to the surface, so a durability of the material is poor.

SUMMARY

40 [0005] A purpose of the present invention is to provide an antibacterial polycarbonate composite, which has advantages of a good appearance, a good color stability, a good antibacterial performance, a gradually increasing concentration of silver ions from inside to outside in the material and a well sustained antibacterial effect which can be maintained since the silver ions inside the material will migrate slowly with attrition of the material surface.

[0006] Another purpose of the present invention is to provide a preparation method of the antibacterial polycarbonate composite.

45 [0007] The present invention is realized through the following technical solutions:

An antibacterial polycarbonate composite, includes the following components in parts by weight:

	Polycarbonate	100 parts
	nanometer metal oxide	0.01 - 5 parts
50	silicon-containing high-molecular polymer	0.01 - 5 parts

based on a total weight of the antibacterial polycarbonate composite, a content of a silver ion is 100 - 1200 ppm.

[0008] Preferably, the antibacterial polycarbonate composite includes the following components in parts by weight:

55	polycarbonate	100 parts
	nanometer metal oxide	0.05 - 2.5 parts
	silicon-containing high-molecular polymer	0.1 - 2.5 parts

based on the total weight of the antibacterial polycarbonate composite, the content of the silver ion is 100 - 1200 ppm.

[0009] Polycarbonate resin: the polycarbonate resin of the present invention can be a branched thermoplastic polymer or copolymer obtained by a reaction of dihydroxyl compounds or the dihydroxyl compounds and a small amount of polyhydroxyl compounds with phosgene or dicarbonate. A production method of the polycarbonate resin is not particularly limited, and the polycarbonate resin produced by a phosgene method (an interfacial polymerization method) or a melting method (a trans-esterification method) as known so far can be used. An aromatic dihydroxyl compound is preferably selected as a raw material dihydroxyl compound, and can be exemplified by 2,2-bis (4-hydroxyphenyl) propane (= bisphenol A), tetramethyl bisphenol A, bis (4-hydroxyphenyl)-p-diisopropyl benzene, hydroquinone, resorcinol, 4,4-dihydroxydiphenyl, etc., among which bisphenol A is preferred. A compound in which at least one tetraalkyl phosphonium sulfonate is bonded to the aforementioned aromatic dihydroxyl compound can also be used.

[0010] In the aforementioned, the polycarbonate resin is preferably the aromatic polycarbonate resin derived from 2,2-bis (4-hydroxyphenyl) propane, or an aromatic polycarbonate copolymer derived from 2,2-bis (4-hydroxyphenyl) propane and other aromatic dihydroxyl compounds. The polycarbonate resin may also be a copolymer with the aromatic polycarbonate resin as a main composition, for example, a copolymer with a polymer or oligomer containing a siloxane structure. In addition, a mixture of two or more of the above-mentioned polycarbonate resins can be used. A mono aromatic hydroxyl compound can be used to adjust a molecular weight of the polycarbonate resin, such as m-methyl phenol, p-methyl phenol, m-propyl phenol, p-propyl phenol, p-tert-butyl phenol and p-(long-chain alkyl)-substituted phenols.

[0011] The present invention has no particular limitation on the production method of the polycarbonate resin, and the polycarbonate resin produced by the phosgene method (the interfacial polymerization method) or the melting method (the trans-esterification method) can be used. The polycarbonate resin can also be provided by subjecting the polycarbonate resin produced by the melting method to a post-treatment for adjusting an amount of terminal hydroxyl groups.

[0012] The silver ion is derived from the silver ion antibacterial agent.

[0013] The nanometer metal oxide is at least one selected from the group of zinc oxide, magnesium oxide, calcium oxide, copper oxide, titanium dioxide, silica, alumina, zirconia, cerium oxide and iron oxide, and a particle size (D50) of the nanometer metal oxide is 200 nm to 800 nm; preferably, the nanometer metal oxide is at least one selected from the group of zinc oxide, magnesium oxide, calcium oxide and copper oxide with the particle size (D50) of 200 nm to 800 nm; and more preferably, the nanometer metal oxide is selected from zinc oxide, with the particle size (D50) of 200 nm to 800 nm.

[0014] The silicon-containing high-molecular polymer is at least one selected from siloxane polymers.

[0015] A molecular weight of the siloxane polymer is 150,000 - 350,000; and preferably, the molecular weight of the siloxane polymer is 200,000 - 300,000.

[0016] The antibacterial polycarbonate composite further includes 0 - 2 parts of a color powder in parts by weight.

[0017] The antibacterial polycarbonate composite further includes 0 - 5 parts of at least one of an antioxidant, a lubricant, a weather resistant agent and a release agent in parts by weight. The role of the antioxidant is to prevent the material from oxidation at high temperature during extrusion and granulation.

[0018] A commonly used white color powder includes titanium oxide.

[0019] The present invention has no particular limitation on the production method, a crystallization morphology, an average particle size and the like of titanium oxide.

[0020] The preparation method of the antibacterial polycarbonate composite includes the following steps: the polycarbonate, the nanometer metal oxide, the silicon-containing high-molecular polymer and the silver ion antibacterial agent are mixed evenly in a high-speed mixing machine according to a ratio, then added to a twin-screw extruder, melted and mixed at a temperature of 240°C - 260°C, and then granulated, cooled and dried, to obtain the antibacterial polycarbonate composite.

[0021] In a general silver ion antibacterial polycarbonate, a conventional addition of a flame retardant will affect physical performances of a resin matrix, and also have a negative impact on an activity of the antibacterial agent. Because the flame retardant will promote an invalidation of the silver ions in a process of high temperature and shear, it will bring an unexpected effect to the composition. The antibacterial polycarbonate composite of the present invention is added with a silicon-containing high-molecular polymer, which can achieve a good compatibility with the polycarbonate matrix resin.

[0022] The present invention has the following beneficial effects:

The present invention provides an antibacterial polycarbonate composite. By adding the silver ion antibacterial agent and the nanometer oxide, and then synergizing a dispersion and migration effect of the silicon-containing polymer, it enables the silver ion antibacterial agent to achieve distribution with a gradient increasing concentration from inside of the material to the surface. When the silver ion antibacterial agent on the material surface is attrited, the silver ions inside the material will migrate to the surface at an even rate along with the silicon-containing polymer to achieve a long-lasting

antibacterial effect, which can reduce an added amount of the silver ions. In addition, the silicon-containing polymer has a color-shading effect, and even if the silver ions are reduced to elementary silver, it will not appear grey. Thus, a beautiful white color can be obtained with a small amount of the white color powder. In summary, the antibacterial polycarbonate composite of the present invention has advantages of good and long-lasting antibacterial effect, good appearance, and stable color, etc.

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DETAILED DESCRIPTION

[0023] The present invention is further illustrated by the following embodiments, but the present invention is not limited by the following embodiments.

[0024] Sources of raw materials used in the present invention are as follows, but are not limited by the following raw materials.

Silver ion source: a silver ion antibacterial agent, IKM50G, Zeomic, Japan;
 Zinc oxide A: Mitsubishi, Japan, D50 = 400 nm;
 Zinc oxide B: D50 = 5 micron;
 Calcium oxide: Merck, Germany, D50 = 400 nm;
 Siloxane polymer A: molecular weight 200,000;
 Siloxane polymer B: molecular weight 300,000;
 Siloxane polymer C: molecular weight 150,000;
 Siloxane polymer D: molecular weight 350,000;
 Siloxane polymer E: molecular weight 100,000;
 Siloxane polymer F: molecular weight 500,000;
 Lubricant: POLY TS 30A, Korea Pacific Chemical;
 Antioxidant: 2112, Adeka;
 Color powder: titanium dioxide 2223, Kronos, Germany;

[0025] Preparation method of Embodiments and Comparative Examples: a polycarbonate, a nanometer metal oxide, a silicon-containing high-molecular polymer and a silver ion antibacterial agent were mixed evenly in a high-speed mixing machine according to a ratio, then added to a twin-screw extruder, melted and mixed at a temperature of 240°C - 260°C, and then granulated, cooled and dried, to obtain an antibacterial polycarbonate composite.

[0026] Test methods for each performance:

- (1) Antibacterial effect: GB 21551.2-2010 (film sticking method). Experimental strains are ATCC 6538P and AS 1.90.
- (2) Antibacterial persistence: determination of Ag particle content on an ICP surface.
- (3) Color stability: composition was injection-molded at 300°C - 330°C into a 2.0 mm standard color plate, L value, a value and b value of the color plate of the composition were compared with those of a color standard sample without adding the silver ion antibacterial agent, and color phase was observed; L means black and white, or light and dark, + means kind of white, - means kind of dark; a means red and green, + means kind of red, - means kind of green; b means yellow and blue, + means kind of yellow, - means kind of blue; mere L, a, b are absolute values, and these three values can be used to accurately represent a color point in a three-dimensional stereogram. Correction can be made through a difference of a relative value with a reference point, and a total color difference can be calculated by a formula $\Delta E=[(\Delta L)^2+(\Delta a)^2+(\Delta b)^2]^{1/2}$. The larger ΔE is, the greater a color change is and the poorer the color stability is.
- (4) Silver ion distribution: a plate with a thickness of 2.0 mm was prepared, after liquid nitrogen quenching, silver element distribution in a cross section was measured by EDX, wherein grade 1 represents an obvious gradient distribution, meaning an excellent migration to ensure a sustained antibacterial ability; grade 2 represents a good gradient distribution, at this time, the gradient is not continuous, meaning a good migration, while probably not ensuring a consistent migration rate; grade 3 represents a general gradient distribution, at this time, the gradient appears a fault, meaning a certain degree of migration while appearing an obvious instability; grade 4 represents concentration existed on the surface only, or concentration existed in a center of the fault, without migration, and without the sustained antibacterial ability; grade 1+ is slightly better than grade 1.
- (5) Thermal stability: in an injection molding machine with an injection temperature set to 300°C, after 10 minutes of thermal retention according to injection pressure and injection temperature specified in an internal standard, a sample strip was injection-molded with a tensile strength of ISO standard. A strength retention rate after the thermal retention was calculated after testing, the higher the strength retention rate is, the better the thermal stability is; and the lower the strength retention rate is, the poorer the thermal stability is.
- (6) Silver ion content: An ICP standard curve extrapolation method. Determination of Ag content in the composition

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was carried out by an optical emission spectrum with inductively coupled plasma (ICP-OES). In order to determine a total Ag content, 2 g of the composition to be tested was weighed, treated with 5 ml of nitric acid, and stirred to dissolve, and the solution was supplemented to 100 ml. The ICP standard curve extrapolation method was carried out to calculate the total Ag content.

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Table 1: Distribution ratios (parts by weight) of each component and test results of each performance for Embodiments

	Embo-diment 1	Embo-diment 2	Embo-diment 3	Embo-diment 4	Embo-diment 5	Embo-diment 6	Embo-diment 7	Embo-diment 8	
PC	100	100	100	100	100	100	100	100	
Silver ion content, ppm	400	400	400	400	400	400	400	400	
Zinc oxide A	0.01	0.05	2	3	0.05	0.05	0.05	0.05	
Calcium oxide	-	-	-	-	-	-	-	-	
Siloxane polymer A	1	1	1	1	0.05	0.1	2	5	
Siloxane polymer B	-	-	-	-	-	-	-	-	
Siloxane polymer C	-	-	-	-	-	-	-	-	
Siloxane polymer D	-	-	-	-	-	-	-	-	
Lubricant	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Color powder	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	
Antibacteria 1 effect ATCC 6538P	99.3	99.9	99.9	99.9	97.2	99.9	99.9	96.9	
Antibacteria 1 effect AS 1.90	98.6	99.9	99.9	99.9	96.3	99.9	99.9	97.6	
Silver ion distribution	Grade 3	Grade 1	Grade 1+	Grade 2	Grade 3	Grade 2	Grade 2	Grade 3	
Color stability	L	94.2	93.20	93.70	92.70	92.30	93.09	92.78	93.35
	a	-0.23	-0.48	-0.46	-0.45	-0.38	-0.56	-0.59	-0.46
	b	2.98	2.05	2.00	1.99	3.05	2.03	2.06	2.10
	ΔE	0.983	0.047	0.206	0.478	1.003	0.797	0.682	1.401
Thermal stability, %	88.9	90.4	91.5	90.1	86.7	89.8	89.5	88.3	

Continued to Table 1:

		Embodi- ment 9	Embodi- ment 10	Embodi- ment 11	Embodi- ment 12	Embodi- ment 13	Embodi- ment 14
5	PC	100	100	100	100	100	100
10	Silver ion content, ppm	100	1200	400	400	400	400
15	Zinc oxide A	0.05	0.05	0.05	0.05	0.05	-
20	Calcium oxide	-	-	-	-	-	0.05
25	Siloxane polymer A	1	1	-	-	-	1
30	Siloxane polymer B	-	-	1	-	-	-
35	Siloxane polymer C	-	-	-	1	-	-
40	Siloxane polymer D	-	-	-	-	1	-
45	Lubricant	0.3	0.3	0.3	0.3	0.3	0.3
50	Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1
	Color powder	0.4	0.4	0.4	0.4	0.4	0.4
	Antibacteria l effect ATCC 6538P	95.7	99.9	99.9	99.9	99.9	98.9
	Antibacteria l effect AS 1.90	93.2	99.9	99.9	99.9	99.9	98.9
	Silver ion distribution	Grade 1	Grade 1	Grade 1	Grade 2	Grade 2	Grade 1
	Color stabilit y	L	93.70	89.7	93.4	92.7	93.8
		a	-0.33	-0.42	-0.48	-0.33	-0.42
		b	2.00	3.76	2.07	3.01	1.99
		ΔE	0.032	1.481	0.079	1.317	1.215
	Thermal stability, %	91.0	86.7	90.3	85.46	88.4	89.1

[0027] It can be seen from Embodiment 1 to Embodiment 4 that when an amount of nanometer zinc oxide is in a range of 0.05 - 2.5 parts, each performance is relatively good.

[0028] It can be seen from Embodiment 2 or Embodiment 5 to Embodiment 8 that when an amount of siloxane polymer with a molecular weight of 200,000 - 300,000 is in a range of 0.1 - 2.5 parts, each performance is relatively good.

[0029] It can be seen from Embodiment 2 and Embodiment 11 to Embodiment 13 that when the molecular weight of

the siloxane polymers is in the range of 200,000 - 300,000, each performance is better compared with the siloxane polymers with a molecular weight of 150,000 and 350,000.

[0030] It can be seen from Embodiment 2 and Embodiment 14 that a dispersion effect of the nanometer zinc oxide is relatively good.

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Table 2: Distribution ratios (parts by weight) of each component and test results of each performance for Comparative Examples

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
PC	100	100	100	100	100
Silver ion content, ppm	400	400	400	400	400
Zinc oxide A	-	0.05	-	0.05	0.05
Zinc oxide B	-	-	0.05	-	-
Siloxane polymer A	1	-	1	-	-
Siloxane polymer E				1	
Siloxane polymer F				-	1
Lubricant	0.3	0.3	0.3	0.3	0.3
Antioxidant	0.1	0.1	0.1	0.1	0.1
Color powder	0.4	0.4	0.4	0.4	0.4
Antibacterial effect ATCC 6538P	<90	<90	<90	<90	<90
Antibacterial effect AS 1.90	<90	<90	<90	<90	<90
Silver ion distribution	Grade 4				
Color stability	L	-	90.20	88.9	91.7
	a	-	-0.58	-0.33	-0.43
	b	-	3.05	3.18	3.01
	ΔE	6.09	2.037	5.732	1.46
Thermal stability, %	21.7	34.5	23.6	71.2	78.3

[0031] It can be seen from Embodiment 1 and Comparative Example 1 that the distribution of silver ions, the color stability and the thermal stability can be obviously improved by only adding 0.01 parts of nanometer zinc oxide.

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[0032] It can be seen from Embodiment 2 and Comparative Example 2 that when the siloxane polymers with the molecular weight of 200,000 - 300,000 are not added, each performance is relatively poor.

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[0033] It can be seen from Embodiment 2 and Comparative Example 3 that when the particle size of zinc oxide is larger than nanometer scale (200 - 800 nm), there is no synergistic dispersion effect, and the performance of the PC itself is reduced due to a weak alkalinity of the zinc oxide, resulting that each performance of the product is poor.

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[0034] It can be seen from Comparative Example 4 or Comparative Example 5 that when the molecular weight of the siloxane polymer is 100,000, each performance is relatively poor; when the molecular weight of the siloxane polymer is 500,000, although the color stability is good and the product is relatively white, its thermal stability is poor, especially the silver ion distribution is poor, which can not meet requirements of a long-term sustained antibacterial effect of the present invention.

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Claims

1. An antibacterial polycarbonate composite, **characterized in that**, the antibacterial polycarbonate composite comprises the following components in parts by weight:

polycarbonate	100 parts
nanometer metal oxide	0.01 - 5 parts
silicon-containing high-molecular polymer	0.01 - 5 parts

10 based on a total weight of the antibacterial polycarbonate composite, a content of a silver ion is 100 - 1200 ppm.

2. The antibacterial polycarbonate composite according to claim 1, **characterized in that**, the antibacterial polycarbonate composite comprises the following components in parts by weight:

polycarbonate	100 parts
nanometer metal oxide	0.05 - 2.5 parts
silicon-containing high-molecular polymer	0.1 - 2.5 parts

20 based on the total weight of the antibacterial polycarbonate composite, the content of the silver ion is 100 - 1200 ppm.

3. The antibacterial polycarbonate composite according to claim 1 or claim 2, **characterized in that**, the silver ion is derived from a silver ion antibacterial agent.

25 4. The antibacterial polycarbonate composite according to claim 1 or claim 2, **characterized in that**, the nanometer metal oxide is at least one selected from the group of zinc oxide, magnesium oxide, calcium oxide, copper oxide, titanium dioxide, silica, alumina, zirconia, cerium oxide and iron oxide, and a particle size D50 of the nanometer metal oxide is 200 nm to 800 nm; preferably, the nanometer metal oxide is at least one selected from the group of zinc oxide, magnesium oxide, calcium oxide and copper oxide with the particle size D50 of 200 nm to 800 nm; and more preferably, the nanometer metal oxide is selected from zinc oxide with the particle size D50 of 200 nm to 800 nm.

30 5. The antibacterial polycarbonate composite according to claim 1 or claim 2, **characterized in that**, the silicon-containing high-molecular polymer is at least one selected from siloxane polymers.

35 6. The antibacterial polycarbonate composite according to claim 5, **characterized in that**, a molecular weight of the siloxane polymers is 150,000 - 350,000; and preferably, the molecular weight of the siloxane polymers is 200,000 - 300,000.

40 7. The antibacterial polycarbonate composite according to claim 1 or claim 2, **characterized in that**, the antibacterial polycarbonate composite further comprises 0 - 2 parts of a color powder in parts by weight.

45 8. The antibacterial polycarbonate composite according to claim 1 or claim 2, **characterized in that**, the antibacterial polycarbonate composite further comprises 0 - 5 parts of at least one of an antioxidant, a lubricant, a weather resistant agent and a release agent in parts by weight.

50 9. A preparation method of the antibacterial polycarbonate composite according to claim 3, **characterized in that**, the preparation method comprises the following steps: the polycarbonate, the nanometer metal oxide, the silicon-containing high-molecular polymer and the silver ion antibacterial agent are mixed evenly in a high-speed mixing machine according to a ratio, then added to a twin-screw extruder, melted and mixed at a temperature of 240°C - 260°C, and then granulated, cooled and dried, to obtain the antibacterial polycarbonate composite.

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5	A. CLASSIFICATION OF SUBJECT MATTER C08L 69/00(2006.01)i; C08L 83/04(2006.01)i; C08K 13/02(2006.01)i; C08K 3/22(2006.01)i; C08K 3/015(2018.01)i; C08K 5/00(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC																			
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08L; CO8K																			
15	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																			
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNABS, CNTXT, VEN, USTXT, WOTXT, EPTXT, SIPOABS, DWPI, CNKI; 金发, 丁超, 李明昆, 岑茵, 彭明乐, 艾军伟, 吴俊, 聚碳酸酯, PC, 抗菌, 抗微生物, 银, 金属氧化物, 氧化锌, 氧化钙, 硅氧烷, 硅聚合物, 有机硅, PDMS, 分散, 迁移, 浓度, 梯度, polycarbonate?, PC, polycarbonic 3d ester, antibiotic?, antibiosis??, antiseptics??, antimicrobials??, silver+, argentum+, argent+, metallic? 3d oxide?, metal? 3d oxide?, ZINC 3D OXIDE, ZnO?, calcium 3d oxide, CaO, +silicon+, +siloxane+, PDMS, dispers+, grads																			
25	C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category*</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">PX</td> <td style="padding: 2px;">CN 109553949 A (KINGFA SCIENTIFIC AND TECHNOLOGICAL CO., LTD.) 02 April 2019 (2019-04-02) claims 1-9</td> <td style="padding: 2px;">1-9</td> </tr> <tr> <td style="padding: 2px;">PX</td> <td style="padding: 2px;">CN 109486153 A (KINGFA SCIENCE & TECHNOLOGY CO. et al.) 19 March 2019 (2019-03-19) claims 1-8</td> <td style="padding: 2px;">1-9</td> </tr> <tr> <td style="padding: 2px;">PX</td> <td style="padding: 2px;">CN 109749391 A (KINGFA SCIENTIFIC AND TECHNOLOGICAL CO., LTD.) 14 May 2019 (2019-05-14) claims 1-15</td> <td style="padding: 2px;">1-9</td> </tr> <tr> <td style="padding: 2px;">Y</td> <td style="padding: 2px;">CN 105524444 A (GUANGZHOU DAZHENG ADVANCED MATERIAL TECHNOLOGY CO., LTD.) 27 April 2016 (2016-04-27) description, paragraphs 14 and 21-23</td> <td style="padding: 2px;">1-9</td> </tr> <tr> <td style="padding: 2px;">Y</td> <td style="padding: 2px;">WO 2017109114 A1 (DIANIA TECH LTD.) 29 June 2017 (2017-06-29) description, p. 5, line 30 to p. 6, line 14, p. 11, lines 24 and 25, p. 23, lines 8-11, p. 47, line 20 to p. 48, line 27, and figure 3</td> <td style="padding: 2px;">1-9</td> </tr> </tbody> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	PX	CN 109553949 A (KINGFA SCIENTIFIC AND TECHNOLOGICAL CO., LTD.) 02 April 2019 (2019-04-02) claims 1-9	1-9	PX	CN 109486153 A (KINGFA SCIENCE & TECHNOLOGY CO. et al.) 19 March 2019 (2019-03-19) claims 1-8	1-9	PX	CN 109749391 A (KINGFA SCIENTIFIC AND TECHNOLOGICAL CO., LTD.) 14 May 2019 (2019-05-14) claims 1-15	1-9	Y	CN 105524444 A (GUANGZHOU DAZHENG ADVANCED MATERIAL TECHNOLOGY CO., LTD.) 27 April 2016 (2016-04-27) description, paragraphs 14 and 21-23	1-9	Y	WO 2017109114 A1 (DIANIA TECH LTD.) 29 June 2017 (2017-06-29) description, p. 5, line 30 to p. 6, line 14, p. 11, lines 24 and 25, p. 23, lines 8-11, p. 47, line 20 to p. 48, line 27, and figure 3	1-9
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30	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.																			
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40	Date of the actual completion of the international search 31 December 2019																			
45	Date of mailing of the international search report 15 January 2020																			
50	Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/CN) No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088 China																			
55	Facsimile No. (86-10)62019451 Telephone No. Form PCT/ISA/210 (second sheet) (January 2015)																			

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	Y	CN 106987082 A (GUANGXI RUIGUIHAN AGRICULTURE CO., LTD.) 28 July 2017 (2017-07-28) description, paragraphs 40, 41, 53, and 57	1-9
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5	Patent document cited in search report		Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)
10	CN	109553949	A	02 April 2019		None
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